Polymer Bulletin 12, 499–506 (1984)

Polymer Bulletin

Novel Supercritical Fluid Techniques for Polymer Fractionation and Purification.

2. Fractionation and Characterization of Functional Siloxane Oligomers

Iskender Yılgör and James E. McGrath

Chemistry Department, Polymer Materials and Interfaces Laboratory
Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061, USA
Val J. Krukonis, Phasex Corp., #1 Mill, 85 Factory Street, Nashua, N.H. 03060

Summary

α,ω-carboxypropyl terminated polydimethylsiloxane oligomers (PSX) having molecular weights (Mn) of 2000 and 6400 g/mole respectively were fractionated by using supercritical carbon dioxide. Parent materials and the fractions were characterized by FT-IR spectroscopy, end group titrations and GPC. Polydispersity of each fraction was determined from the analysis of GPC curves. A calibration curve was also plotted by using Mn values from titration and peak elution volumes from GPC. Even without process optimization we were able to obtain fractions having (Mw/Mn) values between 1.1 and 1.3 compared to the parent materials (PSX-2000 and PSX-6400) which showed polydispersities of 1.6 and 2.1 respectively. The ability to prepare such narrow fractions should be of considerable interest both for academic studies as well as for polymeric biomaterials.

Introduction

Functionally terminated low molecular weight oligomers of various kinds have become important starting materials in the synthesis of segmented, block or graft copolymers (1-6). They have found applications in many systems such as thermoplastic elastomers, engineering thermoplastics, high temperature polymers and impact modified thermosets. Techniques used in the preparation of these oligomers, such as, ring-opening, step-growth, free radical or cationic polymerizations often produce materials with a broad molecular weight distribution (MWD), eg., polydispersities in the range of 1.5-2.0, or higher. In some cases living anionic polymerization can also be used in order to achieve narrow MWD oligomers, but for the present time its applicability is limited to only a few specific systems. For example, with siloxanes this involves utilization of the cyclic trimer, mildly promoting solvents and lithium counter-ions (7).

In our laboratories we have been working on the synthesis and characterization of various functionally terminated siloxane oligomers for over five years (4,5). These materials are produced via ring opening polymerization of cyclic siloxane tetramers in the presence of difunctional siloxane end-blockers by using strong acids or bases as the reaction catalysts. Due to the nature of these processes (8) there is always a ring-chain equilibrium in the reaction mixture and also a broad MWD in the oligomers produced. Before their use in the synthesis of various polymeric systems (especially in modified networks) these cyclic species must be removed from the oligomers. In some cases depending on the structure of the siloxane backbone, this separation cannot easily be achieved by vacuum distillation or by other standard methods. Moreover, from the view point of fundamental research, if a segmented copolymer is synthesized from a narrow MWD oligomer it is often possible to derive a better understanding of the structure-property relationships of the resulting materials since an important variable (eg. a broad MWD) is eliminated.

In this paper we will discuss our studies on the fractionation and characterization of polydimethylsiloxane oligomers (Mn 2000-6400), having α,ω-carboxypropyl end groups, by using supercritical carbon dioxide as the extraction fluid (solvent).

Experimental

Functionally terminated siloxane oligomers were synthesized in our laboratories according to the procedures published earlier (3,5).

Fractionation Set-Up and Procedure

A schematic diagram of the experimental set-up used during the fractionations is shown in Figure 1. The system consists of the following basic units:

(i) Gas cylinder
(ii) Compressor
(iii) Stainless steel, heated, extraction vessels
(iv) Collectors (U-tubes)
(v) Temperature and pressure controllers.

During the fractionations a certain amount (10-100 grams) of oligomer is charged into the extraction vessel, typically a 1" or 2" stainless steel tube, 12" long which is fitted with a check valve at the bottom. After being filled, the vessel is connected to the high pressure system. Carbon dioxide gas is supplied from a cylinder at about 1000 psi and 25°C to the suction side of a double end diaphram compressor (Superpressure, Inc.) and is compressed to the desired pressure. The system is capable of operating at pressure levels of 11,000 psi (750 atm). The pressure of the gas pumped to the extractor is controlled by a back pressure regulator (Circle Seal, BPR) which diverts the bulk of the compressed gas back to the suction side of the compressor. This results in an almost pulse free flow to the vessel. The high pressure gas is then heated to the desired temperature, typically to about 40-60°C above its critical temperature ($T_c(CO_2)=31°C$). The supercritical fluid that is pumped continuously through the extractor dissolves the polymer partially to a certain molecular weight level, consistent with the temperature and

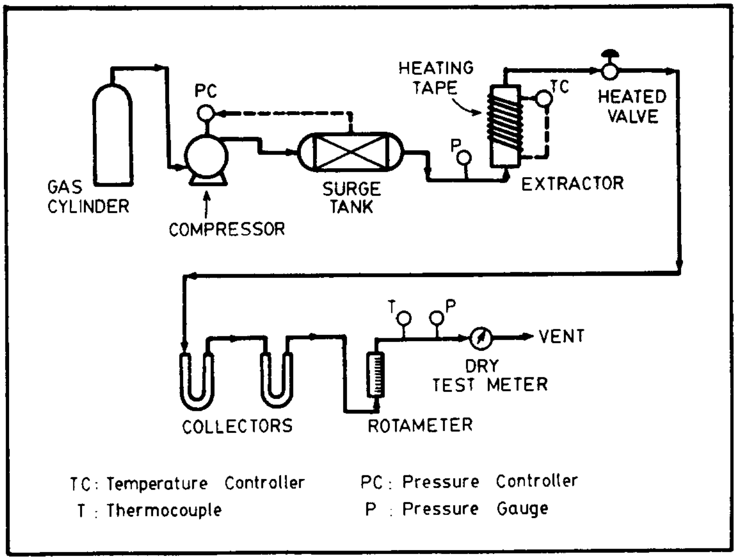

Figure 1. Experimental Set-up Used During Fractionations

pressure in the vessel. Then the solution of oligomer in supercritical carbon dioxide leaves the extractor and passes through a heated, flow-control pressure let-down valve and is expanded to the ambient pressure. Since the solubility of extracted oligomer in carbon dioxide gas at 1 atm pressure is essentially nil, the fraction that has been dissolved in the fluid precipitates down-stream of the pressure let-down valve and is trapped in the collectors. Two 200 mm U-tubes connected in series and immersed in a dry ice-acetone bath (-77°C) serve as the collection system. Generally 99% of the material collected is trapped in the first U-tube. The gas leaves the collection system at ambient conditions, passes through a rotameter for flow rate measurements and through a Dry Test Meter for flow volume integration.

Since the average molecular weight of the fractions solubilized in the supercritical fluid is proportional to the pressure and temperature of the system (9), the procedure described above can be repeated at higher pressures and/or temperatures to obtain higher fractions of the parent material. Therefore by the proper design of experimental conditions and number of stages it is possible to obtain very narrow molecular weight fractions of the parent material. In our fractionation studies the temperature was kept constant at 70°C, but the pressure was increased.

Characterization of the Products

Number average molecular weights (Mn) of the parent oligomers and fractionated components were determined by potentiometric titration of the functional end groups by using Fisher Automatic Titrator II as described earlier (3).

GPC chromatograms were obtained with a Waters 150-C instrument, at 23°C, using THF as solvent and styrogel columns of 10^5, 10^4, 10^3 and 500°A. Flow rate was 1.0 ml/min.

FT-IR spectra were recorded on a Nicolet MX-1 Spectrometer using KBr disks.

Results and Discussion

Functionally terminated polydimethylsiloxane oligomers (PSX) were fractionated by using supercritical carbon dioxide. Each fraction was characterized by titration of the end groups, GPC and FT-IR. GPC curves were later analyzed to determine polydispersity. A calibration curve was also plotted by using Mn obtained from titration and peak elution volumes from GPC.

Tables I and II provide a summary of the results on the fractionation of α,ω-carboxypropyl terminated polydimethyl-siloxane oligomers with Mn 2000 and 6400 g/mole, respectively. As expected, the first fractions in both cases consist of low molecular weight cyclic siloxanes. This is due to the equilibrium nature of siloxane polymerization reactions (8). These cyclic species do not show any titratable (COOH) groups and therefore they are non-functional. FT-IR spectra also does not show any evidence of (COOH) absorption (Figure 2). Other fractions show a gradual increase in Mn as shown from #2 to #7. Accordingly GPC peaks shift to smaller elution volumes. In both extractions overall recovery of the parent material is nearly quantitative. This is given in the second columns of Tables I and II.

Table I

Fractionation of PSX-2000 by Supercritical Carbon Dioxide and Characteristics of Each Fraction

Fraction	% by wt.	Mn (Titr.)	Peak El. Vol. (ml)	Polydisp. (Mw/Mn)
Control	100	2000	37.5	1.63
1	4.0	-	-	-
2	5.2	900	41.1	1.13
3	4.4	1080	40.3	1.20
4	13.0	1500	40.1	1.25
5	20.2	1770	38.7	1.24
6	21.5	2760	36.6	1.16
7	23.0	4100	35.5	1.17

Table II

Fractionation of PSX-6400 by Supercritical Carbon Dioxide and Characteristics of Each Fraction

Fraction	% by wt.	Mn (Titr.)	Peak El. Vol. (ml)	Polydisp. (Mw/Mn)
Control	100	6400	33.8	2.08
1	4.5	-		-
2	5.0	1580	39.4	1.27
3	20.7	3300	36.5	1.42
4	22.2	5700	35.0	1.29
5	11.6	7350	34.0	1.28
6	24.2	10300	33.1	1.27
7	9.0	12850	31.8	1.27

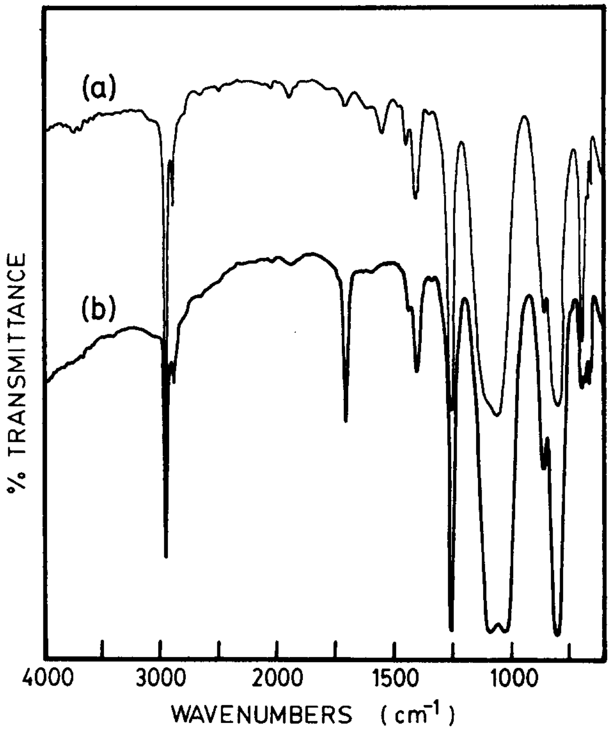

Figure 2. FT-IR Spectra of (a) Fraction #1 and (b) Fraction #2 (see Table I)

GPC traces of PSX-2000 and its fractions are reproduced in Figure 3. The parent material has a polydispersity (Mw/Mn) of 1.63 and hence produces a fairly broad peak. On the other

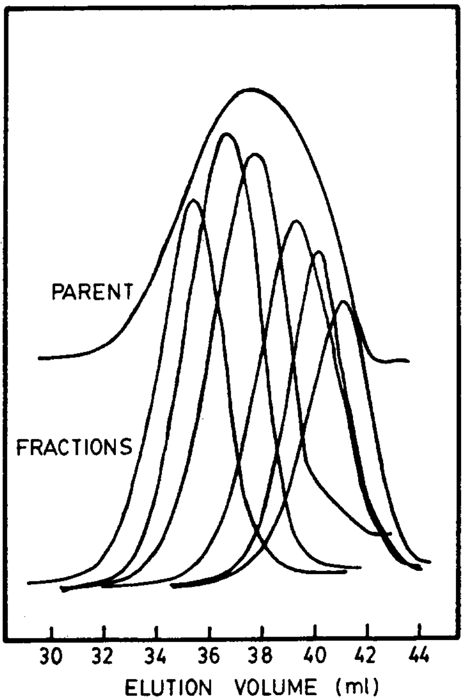

Figure 3. GPC Chromatograms of Carboxypropyl Terminated Polydimethylsiloxane (Mn=2000 g/mole) and its Fractions.

hand, fractions yield very narrow GPC peaks. This demonstrates the efficiency of this supercritical fractionation technique. Polydispersity of each fraction calculated from corresponding peaks and the GPC calibration curves are given in the last column of Table I. The values vary between 1.13 and 1.25 which indicate an effective fractionation. Figure 4 gives the GPC traces of PSX-6400 and its fractions. (Mw/Mn) value for the parent oligomer is 2.08 which indicates a very broad distribution. For the fractions, this value is less than 1.3 which again indicates a reasonably good fractionation (Table II, last column). If this particular oligomer is fractionated into more than 7 fractions, it is, of course, possible to obtain a narrower molecular weight distribution. This has been done on other samples which we will discuss in future publications.

Figure 5 shows the GPC calibration curve constructed for α,ω-carboxypropyl terminated polydimethylsiloxane oligomers by using the (Mn) values obtained from the titration of the end groups and the maxima of peak elution volume of each fraction obtained from GPC. As expected, all the points fall on a straight line with a correlation coefficient of -0.989, which is very good. This is another indication of the effectiveness and potential of supercritical fluid fractionation technique.

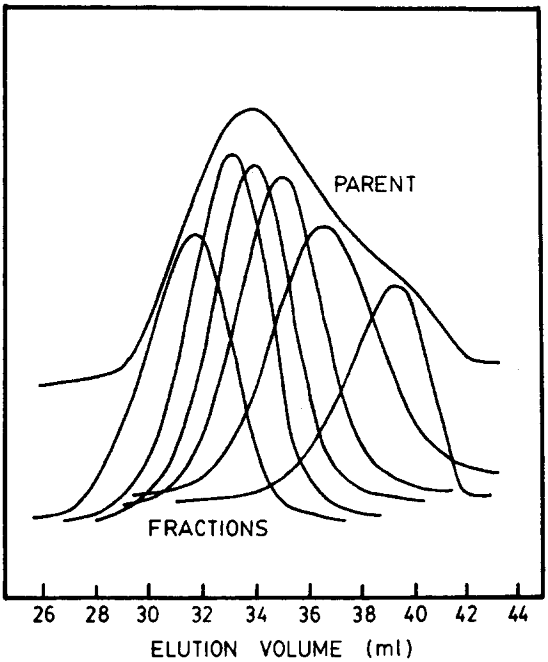

Figure 4. GPC Chromatograms of Carboxypropyl Terminated Polydimethylsiloxane (Mn=6400 g/mole) and its Fractions.

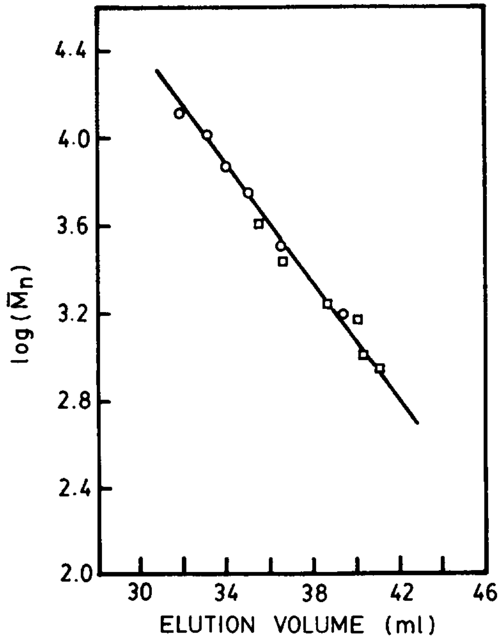

Figure 5. GPC Calibration Curve for Carboxypropyl Terminated Polydimethylsiloxane Oligomers (THF, 23°C, 10^5, 10^4, 10^3, 500°A Styragel Columns).

References

1. Papers presented in "Symposium on Reactive Oligomers", at ACS 187th National Meeting, St. Louis, MO, April 8-13, 1984. See Polym. Prepr., Vol. 25 (1984) and Polymer Materials: Science and Engineering Preprints (PMSE), Vol. 25 (1984); ACS Symposium Series, F. W. Harris, and H. Spinelli, Editors, in press (1984).

2. J. P. Kennedy and E. Marechal, "Carbocationic Polymerization", John Wiley and Sons, New York, 1982.

3. J. E. McGrath, et al., "Epoxy Resin Chemistry II", Ed. R. S. Bauer, ACS Symp. Ser. No. 221 (1983), Ch 2.

4. J. S. Riffle, Ph.D. Thesis, VPI & SU, Blacksburg, VA (1981).

5. İ. Yılgör, et al., Polymeric Materials: Science and Engineering Preprints (PMSE), 50, 518 (1984).

6. J. E. McGrath, Pure and Appl. Chem., Vol. 55, No. 10, p. 1573-81 (1983).

7. A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Critical Survey", Academic Press (1977).

8. J. E. McGrath, J. S. Riffle, A. K. Banthia, İ. Yılgör and G. L. Wilkes in "Initiation of Polymerization", F. E. Bailey Editor, ACS Symposium Series No. 212 (1983), Ch. 13.

9. J. W. King, Polymeric Materials: Science and Engineering Preprints, 51, 707 (1984).

Accepted October 30, 1984